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(54) Title: INFRA-RED TRANSPARENT MATERIALS (57) Abstract Material transparent at infra red wavelengths, 3-5 and 8-14 μm is formed of ZrN, YN, CeN, TLN, or EuN. The material can be used as a self supporting material or as a coating on substrates such as infra red transparent material e.g. Ge, ZnS, ZnSe, As_2S_3 , As_2Se_3 , optically transparent materials e.g. sodium glass, or reflecting surfaces such as metal surfaces, e.g. Al or silvered surfaces. For some substrates e.g. Ge a thin, e.g. 10-1,000 Angstrom bonding layer may be used to improve adhesion. Bonding layers may be Ge, Si, $\text{Ge}_x\text{C}_{1-x}$, $\text{Si}_x\text{C}_{1-x}$ ($0 < x < 1$). The coating may be produced by sputtering in a glow discharge chamber using Ar and N gases.		

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INFRA-RED TRANSPARENT MATERIALS

This invention relates to infra red transparent materials. Such materials are useful as windows and lenses for thermal imaging systems, either as a coating or as a self supporting layer.

- 5 Materials commonly used are germanium, zinc sulphide, and zinc selenide. All are relatively soft and therefore easily damaged. One method of protecting these soft materials is to coat them with a hard material. The coating most successful to date is a hard carbon that is diamond like in its hardness. This is described in
- 10 GB 2,082,562 B. Disadvantages of this material are the interstitial graphitic inclusions which limit the optical transmission and the internal strain which prevents layers thicker than about 1 μm being grown. An alternative coating of hard carbon includes a small amount of germanium to relieve stress and
- 15 allow thicker coatings to be made; this is described in GB 2,129,833 A and its divisional 85 24,696.

- Ideally a hard coating should be transparent in the 3-5 and 8-14 μm infra red wavebands, and also in the visible band i.e. about 0.4 to
- 20 0.7 μm . It is further desirable that the coating is stable and transparent at high temperatures so that it may be used as a window for high temperature processes. A disadvantage of the hard carbon, and hard germanium carbon coatings is their high temperature performance. On heating to say 600°C the carbon
- 25 changes to a graphitic form which is absorbing to infra red radiation. These materials are also absorbing to visible light in useful thicknesses.

- It is an object of this invention to provide a material that is
- 30 infra red transparent over a wide band of wavelengths and elevated temperatures.

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According to this invention an infra red transparent material is formed of Zirconium nitride or Yttrium nitride also Cerium or Thorium or Europium nitride.

5 The material may be used as a coating on infra red transparent substrate material such as Ge, ZnS, ZnSe, AsS₃, AsSe₃; optically transparent material such as sodium, silica or lead glass; any suitable metal such as Cu, Al, alloys of Al, alloys of Fe or silvered surfaces; or as a self supporting layer in which case the
10 supporting substrate is removed e.g. by etching. These infra red transparent materials Ge, etc., are transparent in the 1.9-2.7, 3-5 and 8-14 μm wavebands. ZnS, ZnSe, As₂S₃, As₂Se₃ are also partly transmissive in the visible waveband. Glass is transparent up to about 2.5 μm i.e. the visible and near infra red waveband. The
15 coating is hard and may therefore be used for its abrasion resistant properties for example on infra red windows and lenses. Alternatively it may be used on metal to maintain a highly polished surface on components such as turbine blades and ductings. A further use on metals is to provide a hard wear resistant coating
20 on cutting tools used on lathes etc.

The material may be formed by reactive sputtering using a target of Zr, Y, Ce, Eu or Th in a DC or RF glow discharge of the gases Ar and N.

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According to this invention an optical component comprises a transparent substrate coated with a transparent thin layer of ZrN, YN, CeN, EuN or ThN, the component being transparent in either or both the infra red (1.9-2.7, 3-5 and 8-14 μm) and visible band (0.4
30 to 0.7 μm) of wavelengths.

According to an aspect of this invention a machine tool cutting tip, turbine or pump blade is coated with an abrasion resistant coating of ZrN, YN, CeN, ThN or EuN.

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According to another aspect of this invention the reflecting surfaces of a direct view thermal imager are coated with a thin layer of ZrN, YN, CeN, ThN or EuN.

- 5 According to this invention a method of producing Zirconium, Yttrium, Cerium, Thorium or Europium nitride comprises the steps:-
providing an anode and a cathode inside a vacuum chamber,
arranging a target of Zr, Y, Ce, Th or Eu on the cathode,
mounting a substrate to be coated opposite and spaced from
10 the cathode,
maintaining the substrate at a desired temperature of between 300 and 600°C,
flowing gases of argon and nitrogen through the chamber whilst maintaining a reduced pressure inside the chamber,
15 providing a glow discharge plasma inside the chamber between the anode and cathode whereby argon ions sputter off material from the target to combine with nitrogen on the substrate and form the desired coating.
- 20 The glow discharge may be provided by an R.F. or a D.C. electric field. Enhanced deposition rate may be provided by magnetron sputtering.

- 25 The substrate to be coated may be mounted directly on the anode or spaced therefrom.

- Alternatively the coatings may be grown by molecular beam epitaxy (MBE) growth apparatus, vapour phase epitaxial growth apparatus, or by a ceramic process. In this latter case a powder of Zr, Ce, Th,
30 or Eu nitride is formed and milled to the required particle size, then pressed into a blank of the required shape and fired at an elevated temperature until a ceramic blank is formed.

- 35 Care must be taken in forming the coating otherwise a dark absorbing layer is grown.

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The invention will now be described, by way of example only, with reference to the accompanying drawings of which:-

Figure 1 is a cross sectional view of glow discharge apparatus,

5 Figure 2 is a sectional view of a component coated in the apparatus of figure 1,

Figures 3(a), (b), 4(a), (b) are graphs of transmission against wavelength for the component of figure 2.

10 Figure 5 is a diagrammatic view of a pyro-electric vidicon camera.

As shown in Figure 1 glow discharge apparatus comprises a vacuum tight chamber 1 containing an anode plate 2 and a cathode plate 3. The anode 2 is heated by a heater 4 and carries a substrate 5 to be
15 coated. Examples of substrate materials are Ge, ZnS, Zn Se, and metals such as Cu, Al, silvered surfaces, and various alloys and steels. Both the chamber 1 and anode 2 are connected to earth. The cathode 3 carries a plate of target material 6, e.g. Zirconium (Zr) or Yttrium (Y), and is connected to an RF source 7 via a
20 capacitor 8. Negative voltage developed at the cathode is measured by a D.C. voltmeter 9. Gas bottles 10, 11 supply nitrogen and argon through valves 12, 13, 14 into the chamber 1. A vacuum pump 15 removes gases from inside the chamber 1 via a
25 restrictor valve 16.

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Operation to grow a Zr, or Y nitride layer 17 transparent to a wide band of wavelengths, including the infra red and visible, is as follows: The target 6 and substrate 5 are mounted as shown on the cathode 3 and anode 2 respectively. The anode 2 and substrate 5
5 temperatures are raised to about 500 to 550°C. Other temperatures may be used. However, below about 500°C the grown layer becomes increasingly absorbing. Above about 600°C there are practical difficulties in providing an anode/substrate holder and reliable resistance heaters. The pump 15 is operated to drop the pressure
10 to about 30 millitorr whilst nitrogen and argon gasses are admitted from the bottles 10, 11 and an RF D.C. bias of about -1 kvolts is applied to the cathode. This produces a plasma discharge between the anode 2 and cathode 3. Argon ions strike the target and
15 remove atoms of the target material which combine with nitrogen in the plasma to deposit as a layer 17 of zirconium nitride or yttrium nitride on the substrate 5. For correct deposition parameters the layer is transparent to a wide band of wavelengths e.g. 0.4-16 μ m.

20 Ce, Th or Eu nitride coating layers are grown in a similar manner.

When growing Zr nitride the percentage of N to Ar is about 50%. For Y nitride the percentage of N to Ar is about 1%. Deposition rates are typically 0.2 μ m/hour for ZrN and 0.4 μ m/hour for YN. These rates may be increased by magnetron sputtering techniques.
25

Prior to coating the substrates may be cleaned for example by Ar ion bombardment. This may be achieved by mounting the substrate on the cathode 3, admitting Ar into the chamber whilst reducing the pressure to about 20 millitorr. A glow discharge is initiated and
30 maintained for about 5 minutes. A similar cleaning process may be made to the target 6.

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Coatings of ZrN and YN have excellent adhesion to most metals, e.g. Al, Duraluminium, Cu, stainless steel and Ag. The adhesion on Ge, ZnSe, and ZnS is good but less than for the metals. To improve adhesion on Ge, ZnSe, and ZnS, a very thin bonding layer (less than 0.5 μm) of $\text{Ge}_x\text{C}_{1-x}$ ($0 < x < 1$) may be deposited from a vapour of Ge and C. Typically only a few Angstroms thick layer is needed. For example the bonding layer may be 10 to 1,000 typically 100 Angstroms thick. Being so thin the bonding layer has negligible effect on transmission at any wavelength. The Ge and C vapour may be produced in the apparatus of Figure 1 using a glow discharge to dissociate germane and hydrocarbon gases, without sputtering from a Zr or Y target. Other bonding materials are Ge, Si, and $\text{Si}_x\text{C}_{1-x}$ produced as for GeC. Silicon alone, with carbon, or as an oxide may be used. This can be deposited using a silane feedstock.

Figures 3(a), (b) show the transmittance values for a Ge substrate and for a Ge substrate coated with 0.5 μm of ZrN, the coated substrate being the upper trace. Figures 4(a), (b) show transmittance values for Ge and Ge coated with a 1 μm thick layer of YN. Both Figures 3 and 4 show excellent transmittance from 2.5 μm out to 12 μm and 14 μm for ZrN and YN respectively.

Coating thickness for anti-reflection properties can be calculated as follows:

$$2n_1d = \lambda/2$$

where n_1 is refractive index of coating

d is coating thickness

λ is wavelength of radiation concerned.

For good matching $n_1 = \sqrt{n_0 \times n_2}$

where n_0 and n_2 are the refractive indexes of the material either side of the coatings. For air $n_0 = 1$, for bulk Ge $n_2 = 4$.

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The refractive index was found to be 2.1 for both ZrN and YN which is ideal for use as an antireflection coating on Ge lenses. For use in 8 - 14 μm thermal imagers the antireflection coating would be 1.2 μm thick for a $\lambda/4$ thickness at 10 μm wavelength.

5

The coatings were found to be chemically inert and very hard, having a hardness value >2000 Knoop. This approaches that of diamond-like carbon coatings of the prior art. Unlike these diamond-like coating the ZrN and YN coatings are stable at

10

temperatures in excess of 500 C for long periods.

These properties make the coating useful as windows on tanks and other vehicles where the combination of windsreen wipers and sand make it essential that very hard coatings are used. Behind these windows thermal imagers are arranged to view the thermal scene. Prior to the introduction of hard carbon coatings the lifetime of such windows was very short. An advantage of coatings of the present invention over hard carbon coatings is their optical transparency. This allows both thermal and optical imaging systems to be arranged behind the windows of optically and infra-red transmitting material, e.g. ZnS , $ZnSe$, As_2S_3 , As_2Se_3 window.

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The refractive index of ZnN , YN at about 2.1 is similar to that of ZnS , $ZnSe$, and sodium glasses. Thus coatings directly on such substrates are protective without being anti-reflective. To provide anti-reflective properties a multi coated layer must be used. For example on ZnS or $ZnSe$ substrates a GeC $\lambda/4$ layer with an $n \approx 3$ may be used directly on the substrate. As taught in GB 2,129,833 the value of n is variable with the ratio of Ge to C. Next a layer of GeC with a graded refractive index (effective $n = 4$) is used by varying the Ge:C ratio. The final layer is of a $\lambda/4$ thickness (e.g. 1.2 μm at 10 μm wavelength) of ZnN , or YN .

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Alternatively on ZnS, ZnSe substrates a thick coating, e.g. up to 20 um or more, may be used. This thick coating gives added mechanical protection. A final anti-reflection coating of ThF may be deposited. This is not very hard but for some applications gives an adequate protection.

Another use of the coatings of the present invention is as a front coating on Ge lenses. Figure 5 shows a pyroelectric vidicon camera used by fire fighting services to see through smoke inside burning buildings. These known cameras 20 have a front Ge lens 21 plus other smaller lenses 22 focussing the thermal scene onto a pyroelectric detector tube 23. Output from the tube 23 is used by control circuits 24 to modulate a cathode ray tube (CRT) 25 and form a visible display 26 of the thermal scene. The front lens 21 is coated with ZrN or YN so that dirt is easily removed without damaging the soft Ge material.

Similarly the front lens of optical cameras used in surveying sewers etc may be coated with ZrN or YN to prevent damage.

The high temperature stability enables the material to be used on windows subject to adverse conditions such as in furnaces etc.

Another use of the invention is in direct view thermal imagers. These are known imagers, e.g. G.B. 2,291,196 A, having rotating polygons and/or flapping mirrors to sweep scan the image of a thermal scene onto an infra red detector. Output from the detector modulates the light output from a lamp such as a light emitting diode (LED). The rotating polygons and/or flapping mirror also scans the LED into an eye piece for observation by an operator. The scanning mechanism is thus used to scan infra red and visible light.

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- A problem with rotating polygons is tarnishing of the highly polished reflecting surfaces. One solution to this problem is disclosed in G.B. 2,067,304. A thin layer of infra red transparent amorphous carbon is deposited on the reflecting surfaces. Such a solution is only useful in standard imagers where the detector output modulates a C.R.T. display. The hard carbon is opaque to visible light. Therefore it cannot be used in direct view thermal imagers.
- 5
- 10 However this problem can be overcome by use of the present invention. Reflecting surfaces are protected by a thin coating of ZnN, YN, CeN, ThN or EuN, transparent at infra red and optical wavelengths. The coating may be less than 1 μm - typically about 0.1 to 0.2 μm thick.
- 15
- Self supporting thick, e.g. 10 to 1000 μm or more, layers may be grown e.g. on Al substrates, and the substrate subsequently removed by an etchant such as nitric acid, or hydrochloric acid.

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Claims

1. A material infra red transparent at 3-5 and 8-14 μm wavebands in layer, sheet or bulk form of Zirconium nitride, Yttrium nitride, Cerium nitride, Thorium nitride, or Europium nitride.
- 5 2. An optical component formed of an infra red transparent substrate coated on at least one surface with the material of claim 1.
- 10 3. The component of claim 2 wherein the substrate is Ge, ZnS, ZnSe, As_2S_3 , As_2Se_3 .
- 15 4. The component of claim 2 wherein a bonding layer less than 0.5 μm thick is formed on the substrate, with the coating on top of the bonding layer.
5. The component of claim 4 wherein the bonding layer is of Ge, Si, $\text{Ge}_x\text{C}_{1-x}$ or $\text{Si}_x\text{C}_{1-x}$, $0 < x < 1$.
- 20 6. An optical component formed of an optically transparent substrate coated on at least one surface with the material of claim 1.
- 25 7. The component of claim 6 wherein the substrate is sodium glass.
8. The component of claims 2 wherein the coating has a thickness giving an anti-reflective coating at a specified wavelength.
- 30 9. An infra-red and optically reflecting element comprising a highly reflecting surface coated with the material of claim 1.

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10. The element of claim 9 wherein the highly reflecting surface is a metallic surface and the coating is a layer less than 1 μm thick.

5 11. A method of producing the material of claim 1 comprising the steps:-

providing an anode and a cathode inside a vacuum chamber,
arranging a target of Zr, Y, Ce, Th or Eu on the cathode,
10 mounting a substrate to be coated opposite and spaced from the cathode,

maintaining the substrate at a desired temperature of between 300 and 600°C,

flowing gases of argon and nitrogen through the chamber whilst maintaining a reduced pressure inside the chamber,

15 providing a glow discharge plasma inside the chamber between the anode and cathode whereby argon ions sputter off material from the target to combine with nitrogen on the substrate and form the desired coating transparent to visible and infra red wavelength of 3-5 and 8-14 μm .

20

12. The method of claim 11 wherein, prior to growing the coating, a bonding layer of Ge, Si, $\text{Ge}_x\text{C}_{1-x}$, or $\text{Si}_x\text{C}_{1-x}$ of thickness less than 0.5 μm is grown, $0 < x < 1$.

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Fig. 1.

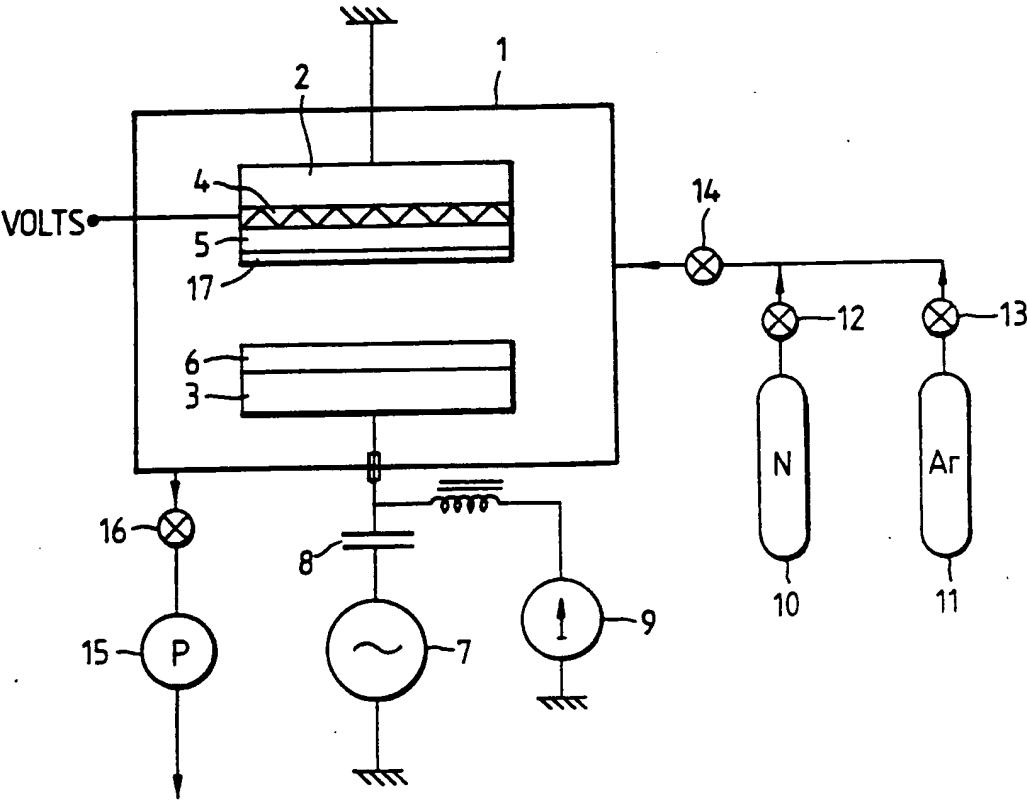
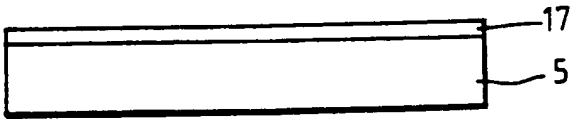


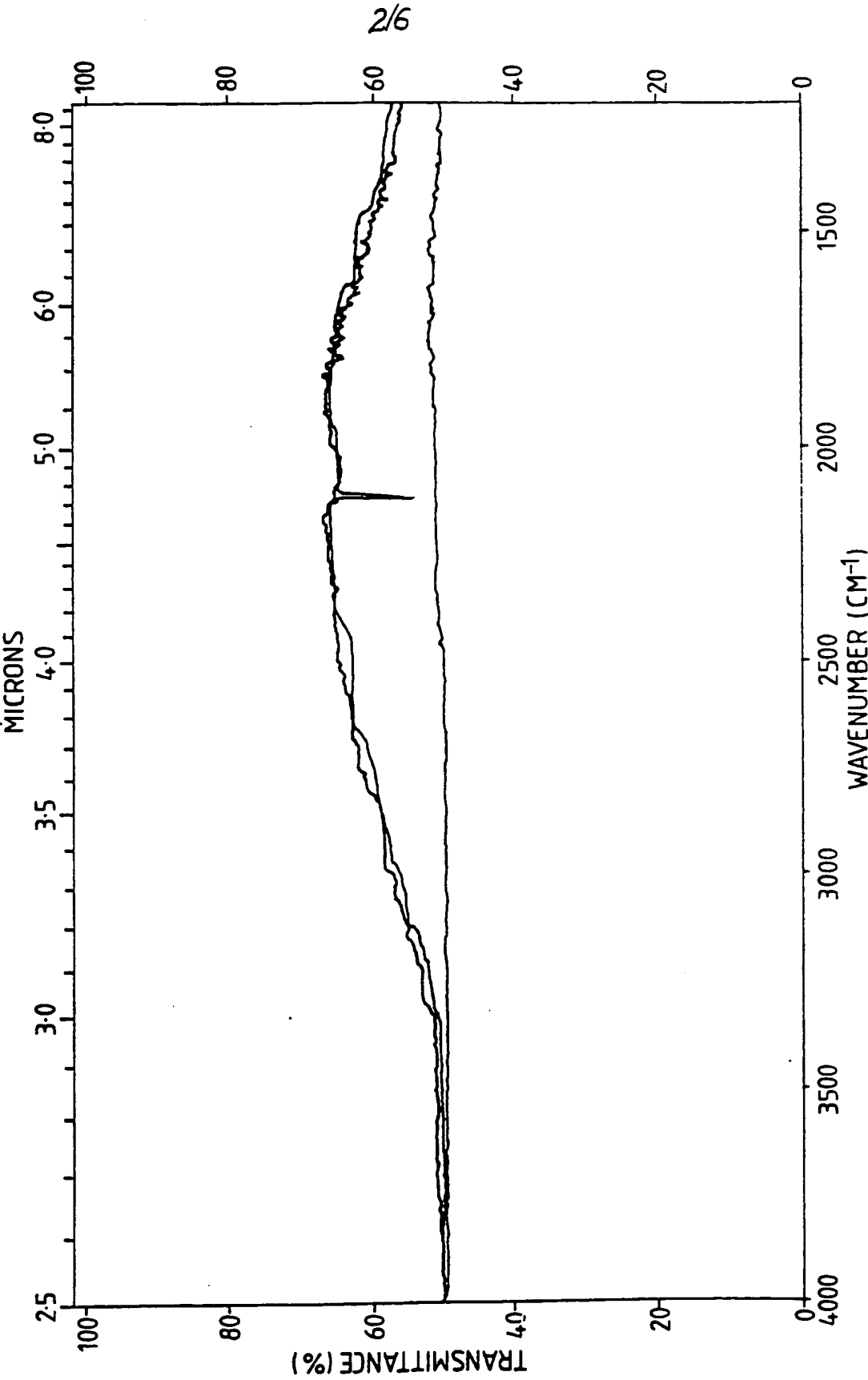
Fig. 2.



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Fig. 3a.



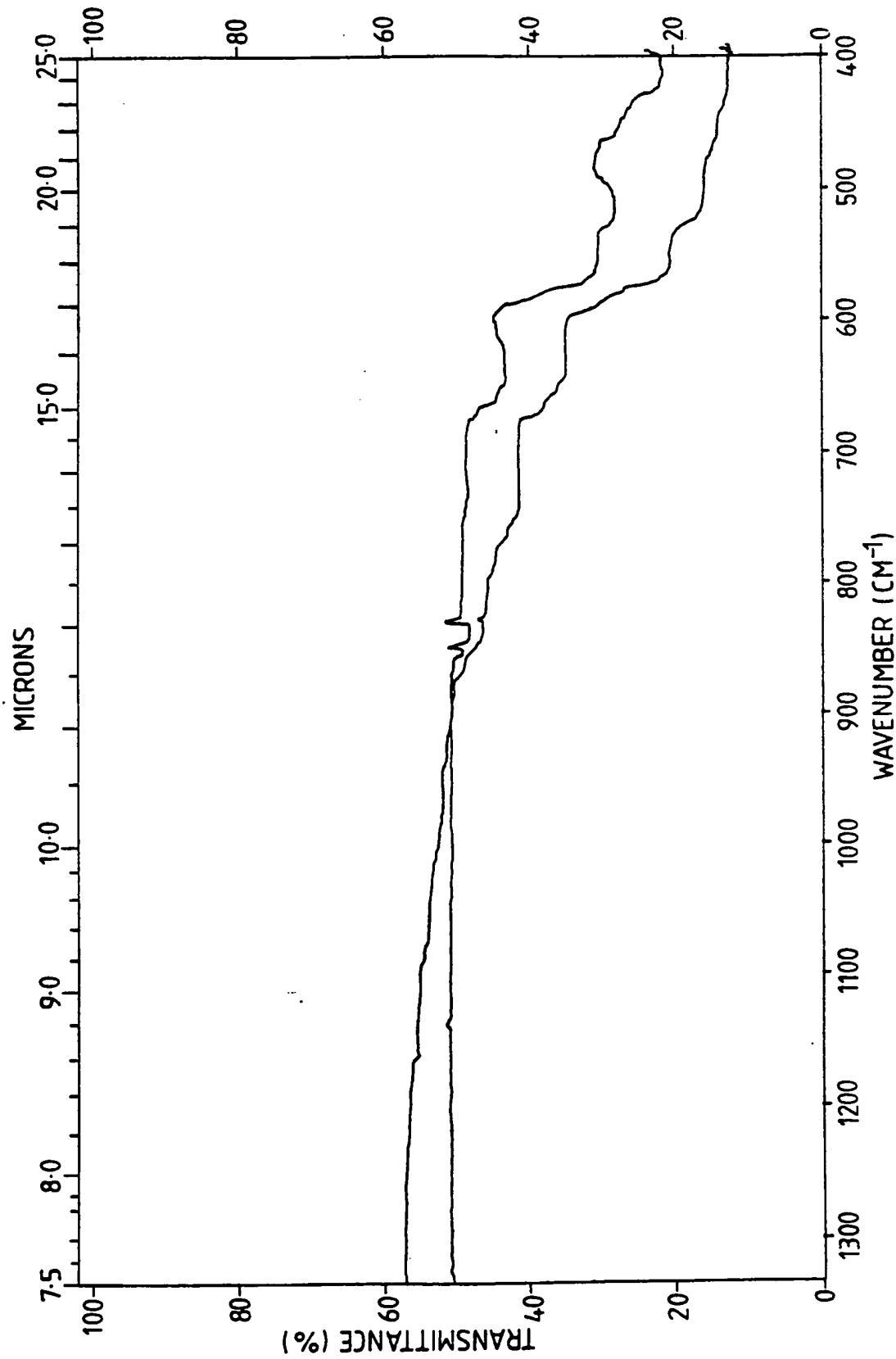
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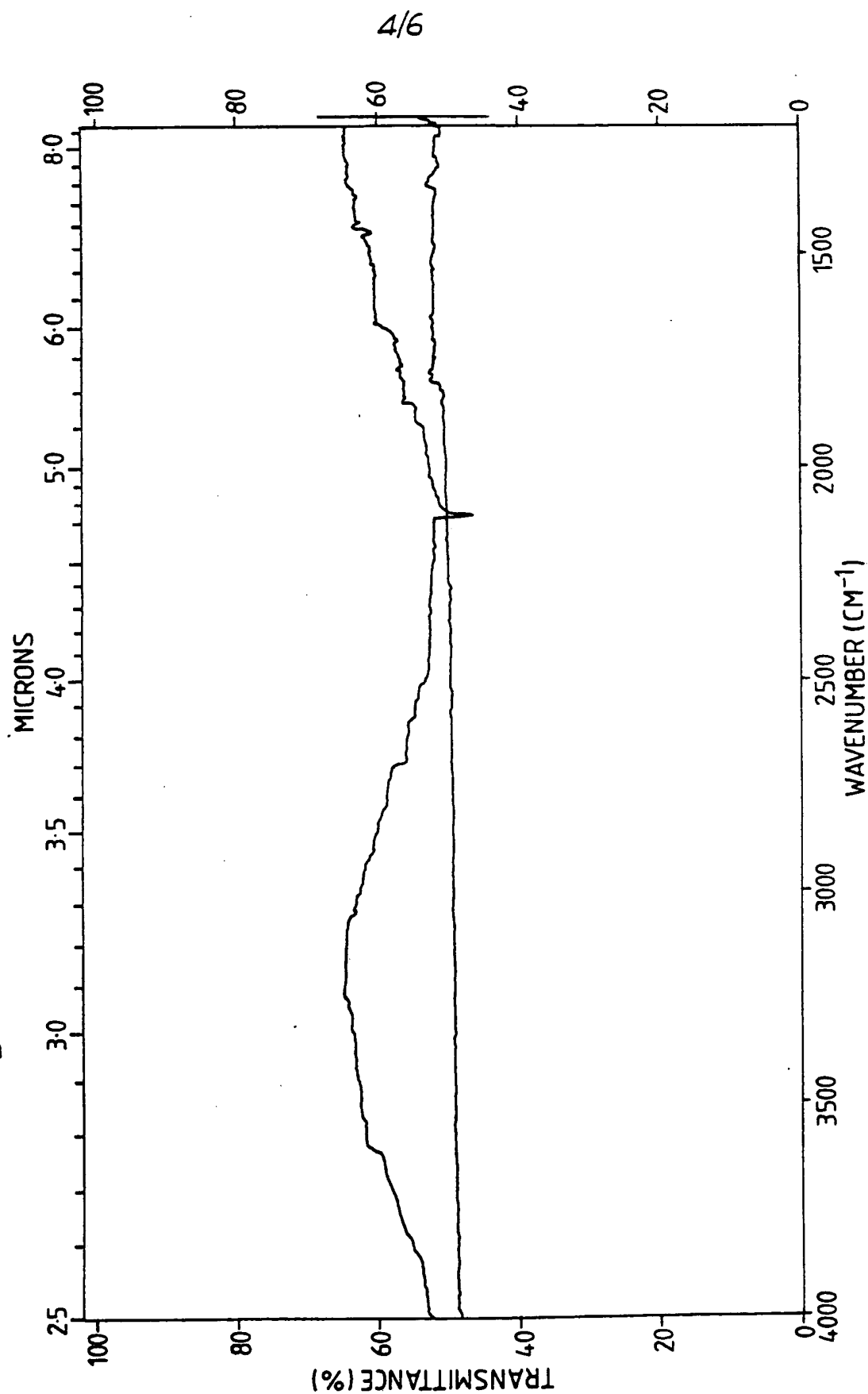
Fig. 3b.



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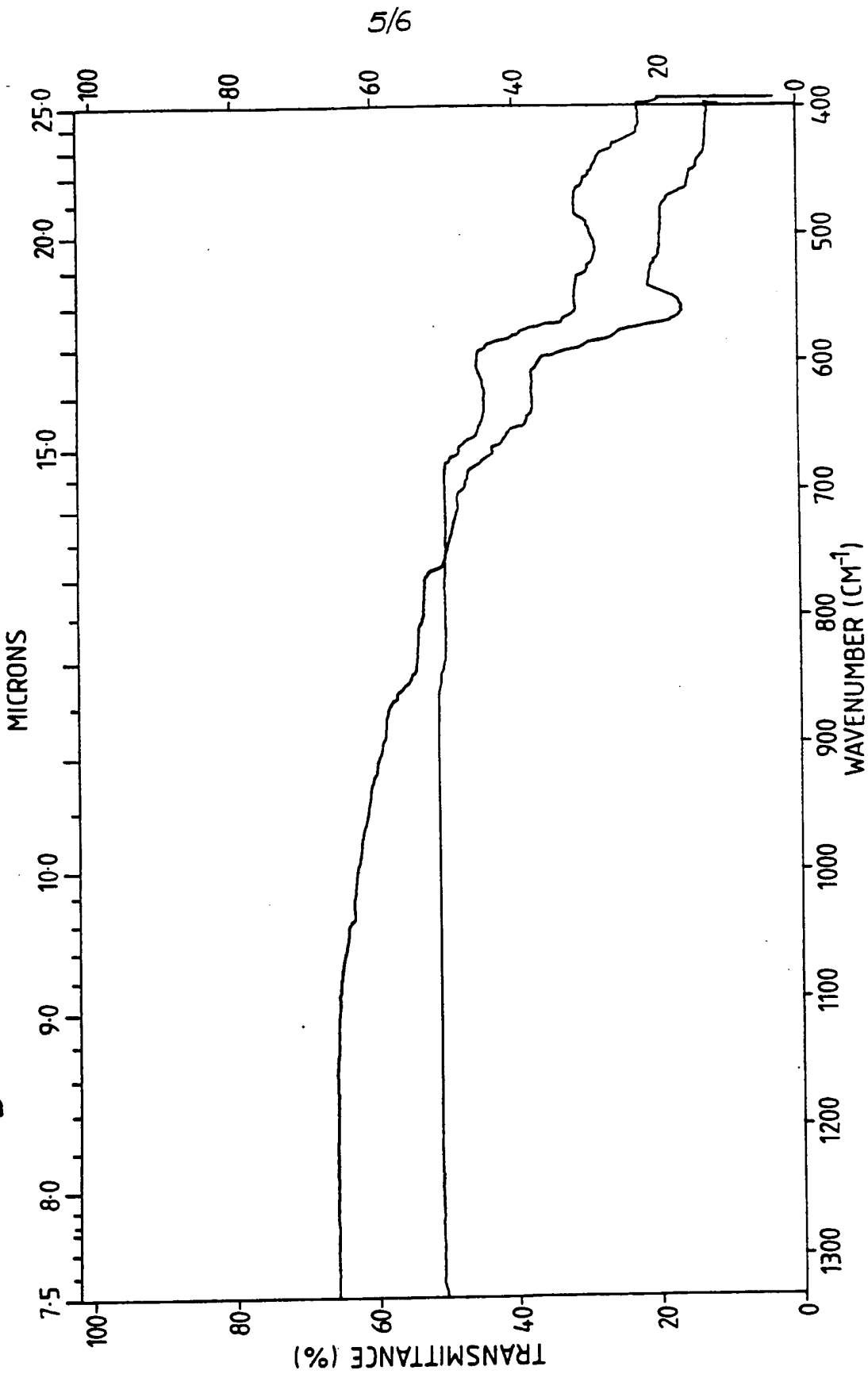
Fig. 4a.

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Fig. 4b.



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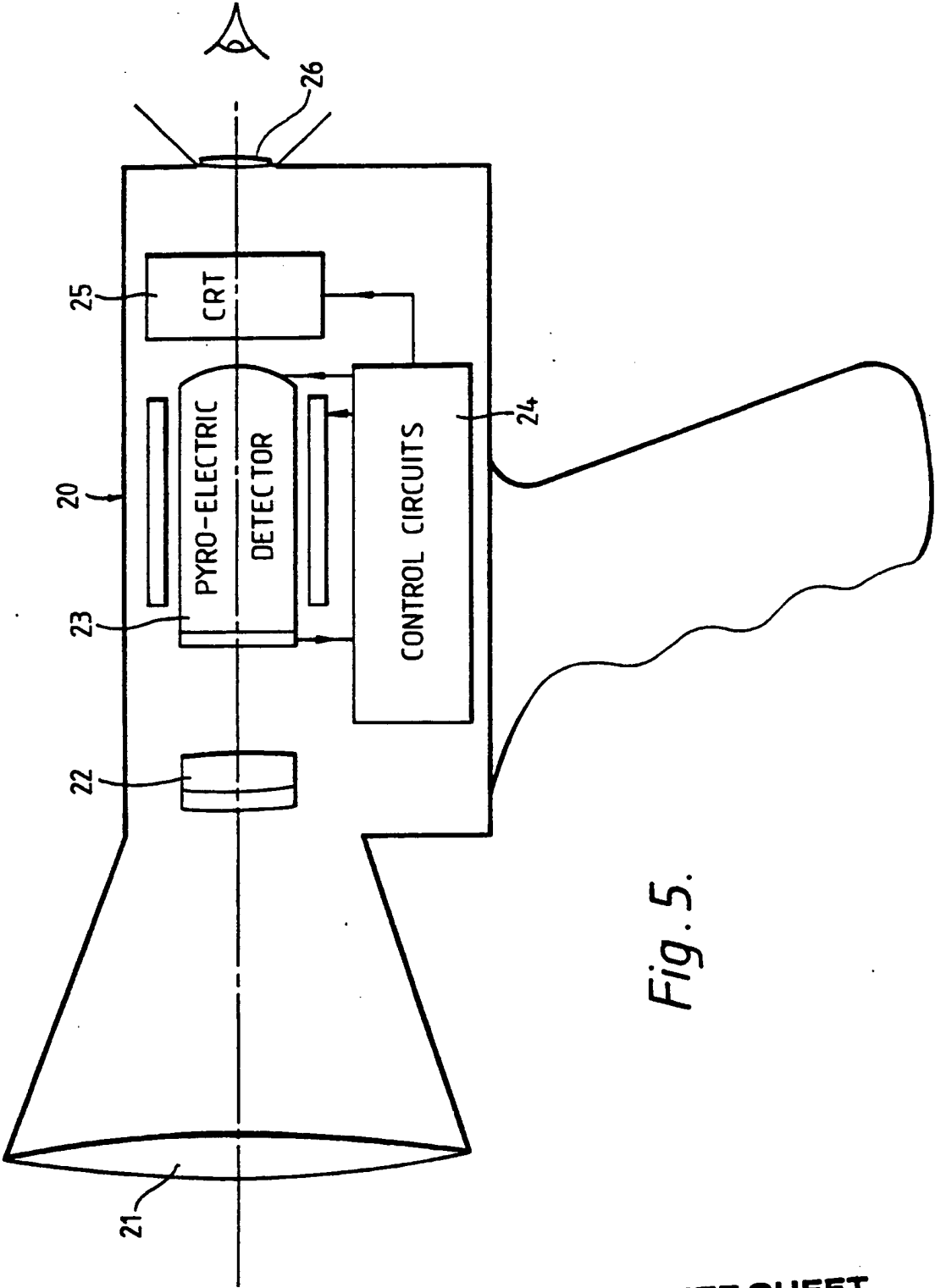


Fig. 5.

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International Application No PCT/GB 89/00068

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A	Solar Energy, vol. 19, 1977 Pergamon Press (GB) R. Blickensderfer et al.: "Spectral reflectance of TiN _x and ZrN _x films as selective solar absorbers", pages 429- 432, see page 429, paragraphs 4,9 --	1,6,7,9-11
A	Solar Energy Materials, vol. 14, no. 3-5, November 1986, North-Holland Physics Publishing Division, Amsterdam (NL) A.M. Bonnot et al.: "Reactively sputtered zirconium carbides. Carbonitrides and nitrides thin films-optical properties" pages 375-384, see page 377, section 3.1; figure 2 --	1,11
A	GB, A, 2165266 (NATIONAL RESEARCH DEVELOPMENT CORPORATION (UK) 9 April 1986, see abstract (cited in the application) -----	3,5,8,12
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